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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

MASS SPECTROMETRIC STUDIES ON POLYPHENYLS

PART II
THE MASS SPECTRA OF THE TRIPHENYLBENZENES AND TRIPHENYLENE

by

S. FACCHETTI, A. COPET and W. BEYRICH

1966

ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Analytical and Inorganic Chemistry

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MASS SPECTROMETRIC STUDIES ON POLYPHENYLS

PART II

THE MASS SPECTRA OF THE TRIPHENYLBENZENES AND TRIPHENYLENE (*)

1 — INTRODUCTION

The interest in the application of mass spectrometric techniques to study the behaviour of proposed organic coolants under electron bombardment has been previously underlined [1]. This investigation has been extended to related compounds that have been found in the products of radiolysis and pyrolysis of terphenyls [2] : triphenylene and triphenylbenzenes. With their molecular mass 228 and 306 respectively these compounds contribute to the formation of peaks that could belong to terphenyls and quaterphenyls.

The interest of presenting complete mass spectral data is increased by the fact that, to our knowledge, no complete spectra of the 3 isomeric triphenylbenzenes have been published and that the spectrum of triphenylene reported in the API catalog of Mass Spectra under serial No. 1018 contains a peak at m/e 217 which belongs to an impurity as shown recently also by M.E. Wacks [3].

2 — SAMPLES

We are indebted to Dr. F. Geiss of the Organic Chemical Division of Euratom, Ispra, who has supplied the samples [4,5] adequately purified by chromatographic techniques. In every case, the purity was higher than 99 % and this was confirmed by low voltage mass spectra.

3 — EXPERIMENTAL

The mass spectra were obtained by means of an ATLAS type CH4 Mass Spectrometer equipped with a high temperature inlet system for the direct introduction of solid samples.

The inlet system and the ion source were operated at 260 °C and 300 °C respectively.

The spectra were recorded at different electron energies from 70 to 10 eV; in accordance with API spectra only those at 70 and 50 eV are reported and discussed here. The low voltage spectra have been handled for quantitative analytical purposes and will be published in another paper.

(*) Manuscript received on December 23, 1965.

An electron ionizing current of 33 microamps and an ion accelerating voltage of 3 kV were used.

4 — SPECTRA OBTAINED WITH ELECTRON ENERGY OF 70 AND 50 eV

The complete mass spectral data are compiled in Table I : the first column indicating the number of C-atoms of the fragment ions, the second the mass to charge ratio, the other ones the relative intensities followed by abbreviations describing the type of certain peaks.

Due to uncertainties in correction for background, the relative intensities of the peak at mass 28 have not been reported, they are in any case inferior to 0.2 %.

The quantity of CO_2 formed by eventual combustion of the sample in the introduction system was small and inferior to 2 % (relative to molecular peak).

5 — DISCUSSION

As for the polyphenyls studied before [1], the spectra are characterized by an intense molecular peak, the highest for every molecule, and by the presence of double and triple charged ions.

5.1 — Molecular stability

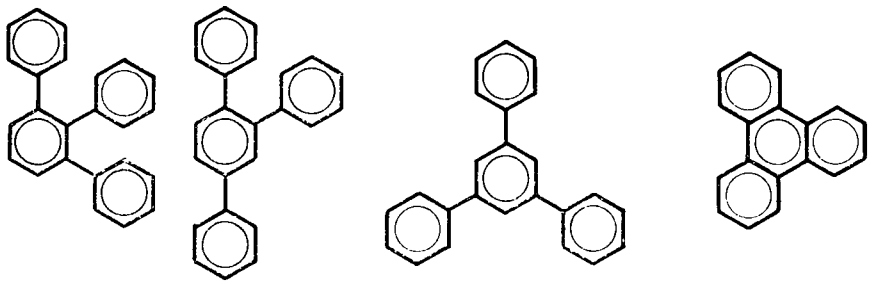
The stability of the molecules against electron bombardment has been expressed (Table II) as the ratio of the height of the molecular peaks to the sum of all peaks of the spectrum. By molecular peak we understand

$$I\ (P) = \sum_{k=0}^{2} I\ (p + k)_{corr.}$$

where p is the mass number of the molecular peak, with its intensity corrected for isotopic contributions of fragment ions.

TABLE I

Mass spectra



Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
2 C	26								0.05		
	27	0.2							0.05		
3 C	38	0.25	0.3	0.1	0.15				0.05		
	39	0.85	1.05	0.45	0.6	0.15	0.1		0.15	0.1	
4 C	50	0.85	1.1	0.4	0.65	0.1	0.05		0.15	0.1	
	51	1.4	1.6	0.8	1.0	0.35	0.2		0.2	0.1	
	52	1.0	1.45	0.45	0.8	0.1	0.05		0.05	0.05	
	53	0.15	0.15	0.05	0.05						
5 C	61								0.05		
	62	0.1	0.05	0.1	0.05	0.05			0.15	0.05	
	63	0.45	0.35	0.4	0.2	0.2	0.1		0.3	0.2	
	65	0.15	0.1	0.15	0.1	0.1	0.05				
	73	0.1	0.1	0.05	0.05				0.05		
	73.5								0.05		d
	74	0.4	0.4	0.25	0.25	0.1	0.05		0.4	0.15	
	74.3								0.05		t
	74.5								0.05		d
	74.7								0.1		t
6 C	75	0.4	0.3	0.25	0.2	0.15	0.05		0.8	0.35	
	75.3								0.55	0.05	t
	75.5								0.75	0.05	d

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	75.7								0.15		t
	76	0.6	0.6	0.35	0.4	0.2	0.15		0.45	0.25	
	76.3								0.05		t
6 C	77	2.55	3.1	1.35	1.9	0.5	0.45		0.1	0.15	
	78	6.9	9.5	2.8	5.35	0.25	0.3	r	0.15	0.25	r
	79	0.4	0.6	0.2	0.35			i			
	82								0.05	0.05	
	85								0.05		
	86					0.05			0.2	0.05	
	86.5								0.05		d
	87	0.25		0.2	0.1	0.15	0.05		1.25	0.55	
	87.5								0.3	0.15	d
	88	0.2	0.1	0.25	0.1	0.15	0.05		2.0	1.5	
	88.5								0.3	0.25	d
	89	0.25	0.2	0.25	0.2	0.2	0.15		0.1	0.1	
7 C	89.5								0.05		d
	91	0.85	0.8	0.8	0.8	0.15	0.15				
	92	0.2	0.05	0.2	0.1	0.1					
	93			0.1					0.05		
	93.5	0.1		0.1				d	0.2	0.1	d
	94	0.05		0.15	0.1				0.05	0.05	
	94.5	0.1				0.05		d	0.05		d
	95.5	0.1		0.15				d			
	96	0.1			0.1						
	96.5	0.15						d			
	98	0.1		0.05					0.25	0.1	
	98.5								0.05		d
	99	0.15		0.15		0.05	0.05		1.2	0.4	
	99.5								0.95	0.4	d
8 C	100	0.6	0.1	0.55	0.1	0.25	0.05		4.75	3.3	
	100.3	0.1		0.1				t			
	100.5	0.05		0.05	0.05	0.05		d	1.15	0.85	d
	100.7	0.15		0.15				t			

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	101	0.4	0.25	0.55	0.35	0.45	0.3		5.7	5.3	
	101.3	0.05		0.1				t			
	101.5			0.1	0.05	0.05	0.05	d	1.0	0.9	d
8 C	102	0.35	0.3	0.45	0.35	0.7	0.5		0.1	0.1	
	102.3					0.1	0.05	t			
	103	0.25	0.25	0.2	0.25	0.15	0.2				
	104	0.05	0.05	0.05			0.05				
	105								0.05		
	105.5	0.15		0.15		0.05		d	0.1	0.05	d
	106	0.15		0.1		0.05			0.05	0.05	
	106.5	0.35		0.35	0.1	0.15	0.05	d	0.25	0.15	d
	107	0.1		0.1		0.05			0.05	0.05	
	107.5			0.1		0.05		d			
	110								0.1	0.05	
	111	0.1		0.1		0.05			0.7	0.2	
	111.5	0.1		0.1		0.05		d	1.2	0.5	d
	112	1.75	1.4	0.95	0.75	0.25	0.05		6.95	4.4	
	112.5	0.3	0.05	0.25	0.1	0.15	0.05	d	4.25	3.2	d
	113	1.55	0.85	1.25	0.7	0.9	0.55		16.5	14.3	
	113.5	0.3	0.1	0.25	0.15	0.2	0.15	d	5.75	5.25	d
	114	0.45	0.5	0.35	0.4	0.35	0.35		12.2	12.2	
9 C	114.5			0.05		0.05	0.05	d	2.35	2.3	d
	115	0.45	0.45	0.25	0.3	0.25	0.25		0.25	0.25	
	117	1.25	1.0	0.05	0.1						
	117.5	0.15		0.1				d			
	118	0.35	0.1	0.2	0.05	0.05					
	118.5	0.85	0.2	0.6	0.2	0.25	0.1	d			
	119	0.5	0.2	0.4	0.2	0.15	0.05				
	119.5	1.5	0.95	0.9	0.6	0.45	0.3	d			
	120	0.45	0.3	0.3	0.2	0.1	0.1				
	120.5			0.15	0.1			d			
	122								0.15	0.05	
	123								0.1	0.05	

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	124	0.7		0.4		0.15			0.05	0.05	
	124.5	0.45		0.25	0.1	0.1	0.05	d			
	125	2.5	0.95	1.7	0.75	0.8	0.35		0.05	0.05	
	125.5	0.65	0.25	0.4	0.2	0.2	0.1	d			
	126	1.85	1.35	1.35	1.05	0.9	0.7		0.1	0.1	
	126.5	0.35	0.25	0.25	0.2	0.15	0.1	d			
	127	0.2	0.15	0.2	0.15	0.1	0.1			0.05	
	128	0.15	0.15	0.15	0.15	0.1	0.15				
10 C	130	0.15		0.1		0.05					
	130.5	1.0	0.25	0.55	0.15	0.25	0.05	d			
	131	0.9	0.4	0.5	0.25	0.2	0.15				
	131.5	4.5	3.0	2.35	1.7	1.2	0.9	d			
	132	2.0	1.5	0.95	0.8	0.55	0.4				
	132.5	2.1	1.65	0.9	0.85	0.57	0.45	d			
	133	1.15	1.05	0.55	0.5	0.25	0.25				
	133.5	0.25	0.2	0.1	0.1	0.05	0.05	d			
	134								0.05	0.05	
	135			0.1					0.05	0.05	
	136	0.3		0.2		0.05					
	136.5	0.3		0.15		0.05		d			
	137	2.65	0.8	1.5	0.5	0.65	0.25		0.05	0.05	
	137.5	1.15	0.55	0.65	0.3	0.25	0.15	d			
	138	8.55	6.2	4.7	3.55	2.4	1.9		0.05	0.05	
	138.5	2.85	2.15	1.5	1.25	0.8	0.65	d			
	139	4.0	3.6	1.6	1.55	0.8	0.75		0.1	0.1	
11 C	139.5	0.85	0.8	0.35	0.15	0.15	0.15	d			
	140	0.1	0.1	0.1	0.1	0.05	0.05				
	140.5	0.4	0.1	0.15	0.05	0.05		d			
	143	0.65	0.35	0.25	0.15	0.1	0.05				
	143.5	4.75	3.0	1.95	1.9	0.9	0.65	d			
	144	3.45	2.55	1.5	1.2	0.6	0.45				
	144.5	13.2	10.7	6.65	6.15	3.0	2.7	d			
	145	15.1	13.0	6.25	6.1	1.95	1.8				
	145.5	5.0	4.5	3.6	3.5	0.7	0.7	d			

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	146	0.85	0.7	0.75	0.65	0.15	0.1	i	0.05		
	146.5	0.1	0.05	0.1	0.1			d			
	147								0.05		
	148								0.05	0.05	
	149	1.2	0.25	0.8	0.2	0.25	0.05		0.15	0.2	
	149.5	0.75	0.25	0.45	0.15	0.15	0.05	d			
	150	5.4	2.95	3.45	2.25	1.6	1.0		0.45	0.5	
12 C	150.5	2.2	1.35	1.45	1.0	0.6	0.4	d			
	151	6.65	5.25	4.8	4.2	2.25	1.95		0.2	0.3	
	151.5	2.45	1.95	1.7	1.5	0.7	0.6	d			
	152	3.1	2.8	2.5	2.55	0.8	0.8		0.15	0.2	
	152.5	0.8	0.7	1.1	1.1	0.15	0.15	d			
	153	2.55	2.45	2.75	2.9	4.05	4.25		0.05	0.05	
	153.5	0.6	0.55	0.7	0.65	1.05	1.1	d, i			
	154	0.2	0.2	0.15	0.15	0.15	0.15				
	161								0.1	0.05	
	162					0.05	0.05		0.1	0.1	
	163	0.25	0.25	0.25	0.2	0.15	0.15		0.25	0.25	
13 C	164	0.1	0.1	0.1	0.1	0.05	0.1		0.1	0.1	
	165	0.55	0.6	0.5	0.55	0.3	0.35		0.1	0.1	
	166	0.1	0.1	0.1	0.1	0.05	0.05				
	167	0.1	0.1								
	173								0.1	0.1	
	174	0.15	0.05	0.15	0.1	0.1	0.05		0.55	0.6	
	175	0.2	0.15	0.15	0.15	0.1	0.1		0.35	0.4	
14 C	176	0.5	0.45	0.4	0.4	0.25	0.25		0.4	0.45	
	177	0.15	0.15	0.15	0.15	0.1	0.1		0.1	0.1	
	178	0.5	0.45	0.25	0.3	0.2	0.2		0.1	0.1	
	179	0.2	0.15	0.05	0.05	0.05	0.05				
	185								0.05	0.05	
	186								0.1	0.1	
	187	0.3	0.25	0.3	0.25	0.15	0.15		0.5	0.55	

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
15 C	188	0.2	0.2	0.4	0.15	0.1	0.1		0.25	0.25	
	189	0.7	0.7	0.7	0.7	0.6	0.65		0.35	0.4	
	190	0.1	0.15	0.2	0.15	0.15	0.15	i	0.05	0.05	i
	191	0.35	0.4	0.4	0.4	0.4	0.4				
	192			0.1	0.1	0.05	0.05	i			
	195			0.2	0.05						
	197			0.45	0.1				0.05	0.05	
	198	0.1	0.05	0.15	0.1	0.05	0.05		0.6	0.7	
	199	0.15	0.15	0.15	0.15	0.05	0.05		0.7	0.85	
16 C	200	1.0	1.0	0.85	0.85	0.5	0.55		2.6	3.1	
	201	0.75	0.85	0.8	0.85	0.45	0.45		1.35	1.6	
	202	2.3	2.55	2.3	2.5	1.95	2.0		2.25	2.45	
	203	0.75	0.9	1.15	1.25	0.8	0.9		0.4	0.4	
	204	0.2	0.15	0.6	0.6	0.4	0.45		0.05	0.05	i
	205			0.1	0.1	0.05	0.05				
	207	0.2		0.8	0.8						
	208			0.15	0.2						
	209			0.1	0.1						
	210								0.05		
	211	0.2	0.1	0.15	0.1	0.05	0.05		0.15	0.15	
	212	0.1	0.05	0.1	0.05	0.05	0.05		0.1	0.1	
17 C	213	0.6	0.6	0.55	0.55	0.4	0.4		0.35	0.35	
	214	0.15	0.15	0.15	0.2	0.1	0.15	i	0.05	0.05	i
	215	5.5	5.45	6.55	6.6	1.45	1.55				
	216	1.0	0.95	1.25	1.2	0.25	0.3	i			
	217	0.1	0.05	0.15	0.1	0.05		i			
	221	0.55	0.45						0.05	0.05	
	222	0.1	0.05	0.05	0.05				0.6	0.65	
	223	0.15	0.05	0.15	0.1	0.05	0.05		1.0	1.2	
	224	1.05	0.95	0.8	0.75	0.45	0.45		5.9	7.35	
	225	1.0	1.05	0.8	0.9	0.55	0.55		4.95	6.0	
18 C	226	6.7	7.6	5.75	6.6	3.9	4.5		27.2	30.7	

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	227	3.55	3.9	2.65	3.4	2.25	2.55		12.8	14.6	
	228	7.3	7.75	6.1	6.5	4.35	4.7		100.0	100.0	p
18 C	229	7.35	7.35	6.55	6.65	2.65	2.5		19.2	19.5	i
	230	1.55	2.1	1.35	1.45	0.5	0.55		1.7	1.8	i
	231	0.15	0.25	0.1	0.15	0.05	0.05	i	0.1	0.1	i
	235	0.1	0.05	0.1	0.05						
	236	0.1	0.05	0.1	0.1						
	237	0.7	0.6	0.4	0.35	0.1	0.15				
	238	0.3	0.3	0.2	0.15	0.05	0.05				
19 C	239	2.45	2.6	1.4	1.55	0.55	0.65				
	240	0.7	0.7	0.35	0.4	0.15	0.15				
	241	1.4	1.3	0.9	0.9	0.25	0.25				
	242	0.3	0.25	0.2	0.15	0.05	0.05	i			
	248	0.35	0.2	0.2	0.15	0.05	0.05				
	249	0.3	0.2	0.15	0.15	0.05	0.1				
	250	1.55	1.6	0.75	0.85	0.35	0.4				
20 C	251	0.5	0.55	0.25	0.25	0.1	0.15				
	252	3.8	3.9	1.6	1.5	0.65	0.7				
	253	1.45	1.5	0.45	0.5	0.15	0.15				
	254	0.3	0.2	0.15	0.15	0.05	0.05	i			
	255			0.1	0.05						
	259			0.15	0.05						
	261	0.45	0.4	0.25	0.2	0.1	0.1				
	262	0.25	0.25	0.15	0.15	0.05	0.05				
	263	2.25	2.4	1.2	1.3	0.6	0.7				
21 C	264	0.75	0.9	0.45	0.5	0.2	0.3				
	265	15.3	15.3	1.9	2.3	0.55	0.65				
	266	3.5	3.5	0.5	0.5	0.1	0.15				
	267	0.35	0.35	0.1	0.1	0,05	0.05	i			
	269			0.1	0.1	0.05					
	272	0.2	0.05	0.1	0.05						

Number of C Atoms	m/e	Triphenyl-benzene 1.2.3		Triphenyl-benzene 1.2.4		Triphenyl-benzene 1.3.5		Type of peak	Triphenylene		Type of peak
		70 eV	50 eV	70 eV	50 eV	70 eV	50 eV		70 eV	50 eV	
	273	0.2	0.1	0.1	0.1	0.05	0.05				
	274	1.3	1.3	0.6	0.85	0.35	0.45				
	275	0.6	0.75	0.55	0.55	0.25	0.3				
22 C	276	6.75	7.65	4.1	4.65	2.0	2.25				
	277	5.05	5.5	2.65	3.05	1.2	1.3				
	278	4.65	4.75	2.05	2.2	0.85	0.95				
	279	2.1	1.95	1.1	0.7	0.35	0.4				
	280	0.35	0.35	0.25	0.25	0.05	0.1				
	285	0.1	0.1	0.05	0.1						
	286		0.1		0.05						
	287	1.3	1.6	0.75	0.9	0.35	0.45				
	288	0.9	1.0	0.75	0.7	0.3	0.3				
23 C	289	25.3	25.3	16.9	18.6	7.8	8.75				
	290	18.1	19.0	11.1	12.2	4.05	4.55				
	291	17.1	17.2	16.0	17.4	3.2	3.45				
	292	3.75	3.7	3.7	3.8	0.65	0.75				
	293	0.50	0.35	0.45	0.45	0.05	0.05	i			
	298	0.6	0.6	0.35	0.35	0.2	0.15				
	299	0.45	0.55	0.2	0.3	0.15	0.15				
	300	3.95	4.9	2.6	3.35	1.35	1.75				
	301	2.45	3.0	1.9	2.4	1.05	1.35				
	302	11.8	14.3	9.0	11.2	4.65	5.65				
	303	11.3	12.9	7.9	9.3	4.2	4.9				
24 C	304	7.0	7.6	7.05	8.3	3.2	3.7				
	305	30.8	29.5	17.6	18.2	2.95	3.25				
	306	100.0	100.0	100.0	100.0	100.0	100.0	p			
	307	25.7	25.2	25.7	25.7	26.0	26.1	i			
	308	3.2	3.05	3.1	3.15	3.55	3.3	i			
	309	0.25	0.2	0.25	0.25	0.25	0.25	i			

TABLE II

Molecular stability I(P)/T.I. × 100

Molecules	70 eV	50 eV
Triphenylene	45.4	46.4
Triphenylbenzenes 1.2.3	23.6	25.9
1.2.4	33.0	32.3
1.3.5	54.6	54.3

The relative stability of a molecule is associated to the value of the ratio I(P)/T.I. i.e. the higher the value, the higher is the stability. As far as the triphenylbenzenes are concerned, the stability is related to the isomerism, the ortho position of a ring weakening the bonds in the molecules.

The triphenylene has a stability higher than the molecules containing an ortho-bond but nevertheless inferior to the 1.3.5 structure showing a stability similar to that of m and p terphenyls [1].

5.2 — Fragmentation

The scope in studying the fragmentation, is to find a possibility to differentiate the isomers, bearing in mind their further determination in presence of compounds with equal mass numbers, like terphenyls and quaterphenyls.

5.2.1 *Loss of Hydrogen*

The hydrogen loss processes are studied in the cases of a single and of a few hydrogen atoms. The relative intensities of the fragments lost are represented by the symbols I (P — l) and $\sum_{n=1}^{8}$ I (P—n) respectively and compiled in Table III.

TABLE III

Intensities of fragments produced by hydrogen loss processes

Molecules	70 eV		50 eV	
	I (P—l)/T.I. × 100	$\sum_{n=1}^{8}$ I (P—n)/T.I. × 100	I (P—l)/T.I. × 100	$\sum_{n=1}^{8}$ I (P—n)/T.I. × 100
Triphenylene	3.5	20.7	4.1	24.5
Triphenylbenzenes :				
1.2.3	7.3	14.9	7.8	17.7
1.2.4	5.5	13.7	5.5	15.2
1.3.5	1.2	7.8	1.3	9.2

The triphenylbenzenes with ortho bonds show a preferential loss of hydrogen, as this has been observed on the ortho-isomers of ter- and quaterphenyls [1]. The 1.3.5 triphenylbenzene presents a reduced loss of hydrogen and from first approximations, an equal probability of losing from 1 to 3 atoms with a relatively higher one for 4 H (see Table IV).

For these molecules however the combined loss of hydrogen atoms is not characteristic and in triphenylene it exceeds that of triphenylbenzenes. Particularly important for that molecule is the loss of 2 H as it can be seen in table IV. This preferential behaviour is characteristic of condensed hydrocarbons as shown by the mass spectra of phenanthrene, anthracene, naphtacene, etc. [3,6.]

TABLE IV

Hydrogen lost at 70 eV

Mass number of lost fragment	Atomic composition	Relative intensities (1)			
		Triphenylene	Triphenylbenzenes		
			1.2.3	1.2.4	1.3.5
1	H	3.52	7.30	5.51	1.25
2	2 H	12.13	1.13	1.82	1.24
3	3 H	1.77	2.10	1.94	1.66
4	4 H	2.64	2.86	2.96	2.42
5	5 H	0.42	0.36	0.42	0.39
6	6 H	0.26	0.97	0.88	0.72

(1) Corrected for fragment isotopic contributions and expressed in percent of the total ionization.

Summing up, we can say that :
the loss of 1 H is characteristic for triphenylbenzenes with o-bond;
the loss of 2 H is characteristic for triphenylene;
the loss of 4 H is characteristic for 1.3.5 triphenylbenzene.

5.2.2 *Loss of Carbon*

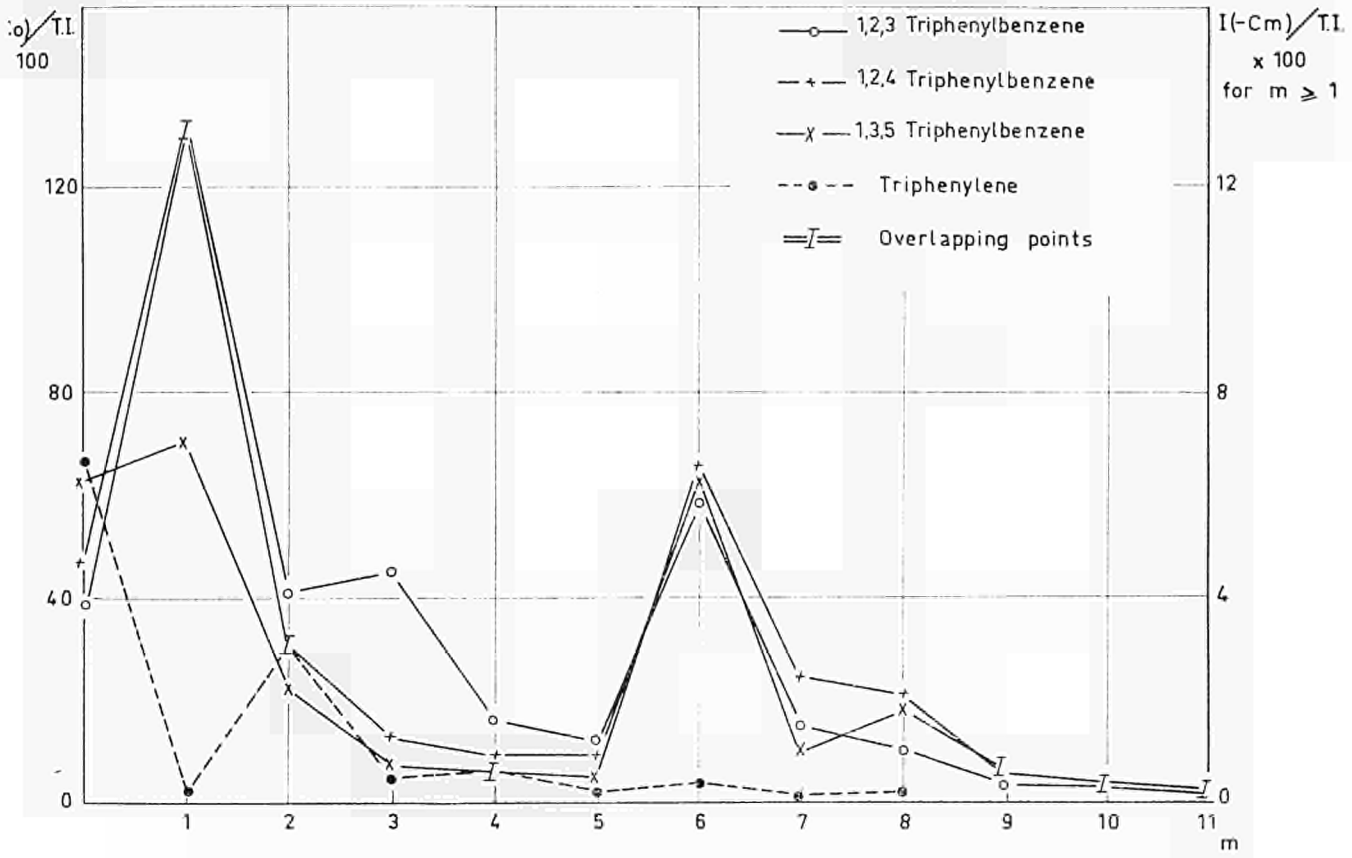
In order to express these processes, we use the "group" ionization defined as the sum of the intensities of all ions formed by the loss of fragments containing 0,1,2... $(\frac{n}{2} - 1)$ carbon atoms, (*) n being the number of carbon of the considered molecule.

(*) As already mentioned in a previous paper [1], the use of this method leads to values which are not directly representative for the total amount of fragments charged and uncharged, with a certain number of carbon atoms. In order to obtain those figures, it would be necessary to separate the ion intensities measured at m/e values below one half of the parent peak into the contributions of single and double charged ions and to add them to the group ionizations of the complementary fragments.
This way has not been followed because of the principal difficulty in accurate distinction between single and double charged ions at whole mass numbers. However an estimation of the double charged ions based on the ratio of the intensities of doubly and monocharged isotopic molecule ions has given the possibility to add the complementary ions to the group ionization I (— Cm) used in the present discussion.
From first approximations, the values computed following the two methods do not appear very much different.

The intensities of these groups are represented by I (— Cm) with m = 0,1,2..., the sign (—) indicating that the fragment is released by the molecule.

In Table V, the values of the "group" ionizations at 70 eV are given, their relative intensities being represented graphically by Fig. 1.

Fig. 1 : RELATIVE GROUP IONIZATIONS I (-Cm)/T.I.



The case of the triphenylene is relatively simple, the more significant "group" ionization being the $-C_2$ which is typical for condensed aromatic hydrocarbons and for benzene [3].

In both molecules, the $-C_2$ group is formed particularly by the C_2H_2, C_2H_3 and C_2H_4 lost fragments. However the main contribution to that group in the triphenylene is given by the (p — 28)-loss of C_2H_4 (see Table VI) —instead of the (p — 26)-loss of C_2H_2 — found for benzene.

TABLE V

Relative group ionization I(-Cm)/TI × 100 at 70 eV

C^m	1.2.3 triphenyl benzene	1.2.4 triphenyl benzene	1.3.5 triphenyl benzene	Triphenylene
C_o	38.5	46.8	62.5	66.2
C_1	13.1	13.2	7.0	0.25
C_2	4.1	3.1	2.2	3.05
C_3	4.5	1.27	0.69	0.51
C_4	1.6	0.89	0.6	0.59
C_5	1.19	0.95	0.46	0.21
C_6	5.8	6.5	6.2	0.41
C_7	1.49	2.4	0.97	0.11
C_8	1.03	2.1	1.79	0.17
C_9	0.33	0.53	0.63	
C_{10}	0.32	0.28	0.34	
C_{11}	0.19	0.25	0.27	

Of the triphenylbenzenes, the 1.2.4 isomer shows a "group ionization" curve qualitatively similar to the curves representing the ortho-quaterphenyls with an inversion for the quantitative abundances of I (— C_1) and I (— C_6).

Contrary to the quaterphenyls, the 3 triphenylbenzenes have the same intensities of I (— C_6). On the I (— C_1) and I (— C_3) values, however, the isomerism has a clear effect : I (— C_3) has the highest value and is therefore typical for the 1.2.3-isomer, I (— C_1) is important for both molecules containing ortho bonds. It is interesting to note, that this last feature has also been observed previously for the ortho-terphenyl and ortho-quaterphenyls [1]. Therefore it seems there is a probability that the ring opening process involved in this fragmentation happens for one ring in the ortho position and that an alkyl phenanthrenic structure is formed, whose stability according to that of similar compounds (triphenylene, phenanthrene, anthracene) is higher. The released carbon atom could be explained as a fragment of the alkyl chain.

Independent of Mass Spectrometry, some experimental facts give evidence for the formation of triphenylene from ortho-terphenyl which has been more intensely studied. It was found in high amount as a by-product in the synthesis (*) of deuterated ortho-terphenyl and also it occurs in the radiolysis of terphenyl coolant [2]. These observations and the evidence of the high stability of triphenylene (see table II) could lead to the assumption that structures of the triphenylene type are also involved in the fragmentation process of the ortho isomers of terphenyl, quaterphenyls and triphenylbenzenes (**).

The most simple process of this kind should be associated with the loss of 2 hydrogen atoms in the terphenyls and the loss of one ring and hydrogen atoms in the other molecules.

(*) Communicated by Dr. F. Geiss and identified by Mass Spectrometry.

(**) Partially discussed at the 27th Congress of GAMS Paris (31st May — 4th June 1965). Considérations sur les spectres de masse de quelques hydrocarbures aromatiques tétracycliques. A. Copet; S. Facchetti.

Even, if the loss of 2 H in the ortho terphenyl compared to the other two isomers is not sufficiently characteristic, this does not exclude the possibility of a competitive formation between phenanthrenic and triphenylenic structures, as hydrogen rearrangement may occur.

As far as quaterphenyls are concerned, the loss of hydrogen associated with the loss of one ring is characteristic for ortho compounds. Therefore by rearrangement of the residual ions, the formation of a triphenylene structure could be considered.

On the contrary, the formation of triphenylene (loss of one ring and hydrogen) does not result from the spectra of the ortho bonded triphenylbenzenes, which have probably a better possibility to form a phenanthrenic structure, as indicated by their specific $-C_1$ loss.

TABLE VI

Fragments lost at 70 eV

Mass number of lost fragments	Atomic composition	Relative intensities (*)			
		Triphenylene	Triphenylbenzenes		
			1.2.3	1.2.4	1.3.5
15	1 C 3 H	0.14	3.35	4.69	1.30
16	1 C 4 H	0.03	2.95	2.36	1.15
17	1 C 5 H	0.07	6.30	5.69	4.19
26	2 C 2 H	0.93	—	—	—
27	2 C 3 H	0.41	0.27	0.25	0.10
28	2 C 4 H	1.12	0.90	0.51	0.32
29	2 C 5 H	0.28	0.86	0.57	0.40
30	2 C 6 H	0.27	1.65	1.34	1.03
41	3 C 5 H	0.22	3.73	0.63	0.29
43	3 C 7 H	0.03	0.55	0.39	0.31
54	4 C 6 H	0.23	0.90	0.44	0.33
56	4 C 8 H	—	0.36	0.23	0.18
65	5 C 5 H	0.10	0.31	0.28	0.09
67	5 C 7 H	0.04	0.59	0.45	0.29
77	6 C 5 H	0.07	1.43	1.75	0.94
78	6 C 6 H	0.18	1.60	1.84	2.04
79	6 C 7 H	0.06	0.53	0.49	0.76
80	6 C 8 H	0.01	1.55	1.82	1.95
91	7 C 7 H	0.27	1.29	2.09	0.72

(*) Corrected for isotopic fragment contributions and expressed in percent of the total ionization.

5.3 — Considerations on the radiolysis products of polyphenyls

Although the comparison between the fragments released by electron bombardment in the source of a mass spectrometer and the products formed by irradiation of polyphenyls has not to be considered rigorously, some comments can be added on the formation of gas and low boilers in the radiolysis of triphenylene and triphenylbenzenes, as would be expected from the mass spectral data.

Hydrogen : according to the data of Table IV, hydrogen will be expected in a greater quantity in the radiolysis of triphenylene than in that of triphenylbenzenes. For the latter compounds, as seen already for ter- and quaterphenyls [1], the production of hydrogen will be favoured by the presence of ortho-bonds in the molecule.

Gaseous hydrocarbons : Methane, according to Table VI, would be produced by the triphenylbenzenes, and as observed for terphenyls and quaterphenyls preferably by the ortho-isomers.

As for production of hydrocarbons with 2 C, triphenylene would have a tendency to produce ethylene and acetylene though the triphenylbenzenes, on the contrary, would form preferentially ethane, and ethylene in the case of the 1.2.3 isomer.

For this last isomer an important formation of a C_3-hydrocarbon would also be expected.

Low Boilers : The formation of low boilers containing 6 C would occur with approximately the same probability for each triphenylbenzene.

The above predictions have not yet been controlled by radiolysis experiments on pure samples.

6 — CONCLUSION

The particular behaviour of molecules having ortho-bonds, as it has been observed for the polyphenyls studied previously, is confirmed by the behaviour of the triphenylbenzenes. This type of compound is characterized by a lower stability under electron impact leading to a greater fragmentation by rupture of C-H and C-C bonds.

The triphenylene like other aromatic hydrocarbons, with condensed structure, is characterized by a high stability and a very specific fragmentation showing a higher probability for the loss of 2 H and of 2 C atoms associated with hydrogen.

The low voltage spectra recorded and the differences shown in fragmentation of the examined molecules will be helpful for their identification in used terphenyl coolants.

7 — ACKNOWLEDGMENT

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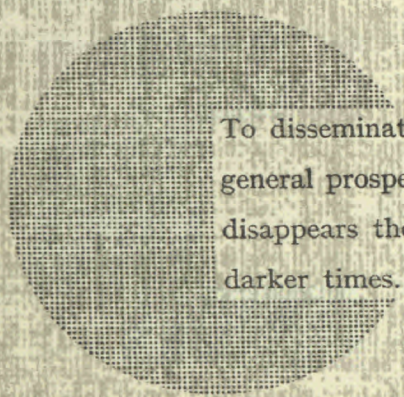

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Alfred Nobel

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